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Published in:
The Journal of Chemical Physics

DOI:
10.1063/1.1671466

Diphenylamino Radical Dimer as a Color Center in a Molecular Crystal

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(Received 8 November 1968)

Radical pairs of diphenylamino (DPA) can be formed in a single crystal of tetraphyenylhydrazine (TPH) by uv photolysis. The structure of these radical dimers can be elucidated by ESR measurements. These studies show that eight configurationally different dimers occur, which fall into two classes with 3- and 4-Å separation, respectively. Optical measurements reveal long-wavelength charge resonance absorptions arising from the dimers; this interpretation is supported by polarization measurements. Temperature-dependent ESR measurements were used to determine the singlet–triplet splittings of the two spin systems, yielding about 130 and 40 cm^{-1} for the 3- and 4-Å dimers, respectively. The radical dimer crystal defect can be regarded as a color center in a molecular crystal.

INTRODUCTION

A considerable amount of work has been reported on radical pairs in solid solution and in the crystalline state.[1] Particularly the enhanced knowledge of the ESR spectra deriving from triplet states has contributed greatly to our understanding of these species.[2]

In a previous paper,[3] we have shown that the photodissociation of tetraphenylhydrazine (TPH) in solid solutions leads to the formation of a diphenylamino (DPA) radical pair. It has now been found that TPH can also be photodissociated in a single crystal of itself, which lends itself to a detailed study of the ESR and optical properties of the radical dimer.

Upon uv irradiation of a single crystal of TPH at 77°K it becomes slightly paramagnetic and assumes a green color. Warming up the crystal to room temperature makes magnetism and color disappear and this process can be repeated indefinitely. We have found that color and magnetism derive from eight configurationally different radical pairs. These pairs have been studied in detail and the results are reported in this paper. After a discussion of the experimental procedures we give an analysis of the ESR spectra found, followed by a discussion of the data. We then turn to the optical spectra, their interpretation, and the polarization measurements, which support this interpretation. Finally, a short discussion is given of the light scattering occurring in these crystals, which is probably due to the introduction of density fluctuations by the dissociation of the TPH molecules.

EXPERIMENTAL

Tetraphenylhydrazine (TPH) obtained from K & K was recrystallized twice from a 1:1 mixture of toluene and chloroform. Single crystals of TPH were obtained by slowly evaporating a saturated solution of TPH in a 1:1 toluene–chloroform mixture.

When the crystallization was performed in a styrofoam box, well-developed transparent single crystals of about 10×5×4 mm were grown, which were used for optical measurements, while smaller crystals were used for ESR studies. Two different crystal shapes were observed, perfectly shaped crystals, where only the C axis of the crystal could be located, others being pyramidal allowing identification of all crystal axes visually.

In our experiments only pyramidally shaped crystals were used. The ESR measurements were performed on a Varian E-3 spectrometer, equipped with low-temperature accessory.

Single crystals of TPH were mounted under a microscope on carefully cut plastic rods ($\phi=3$ mm) which were fixed in another plastic rod ($\phi=10$ mm) that was connected to a disk. The disk was rotated in a Dewar-fixed plastic holder with angular divisions of 1°. To prevent the crystal from being damaged during cooling, the small plastic rod was mounted in a quartz tube, which was fixed inside the Dewar at two points, minimizing deviations from a desired orientation after rotation of the disk. A diagram of the apparatus is shown in Fig. 1. The optical measurements were performed on a Cary-14 spectrophotometer or on a Beckman DK-2A. After polishing, the crystals were mounted in a crystal holder equipped with quartz windows. Then the crystal holder was very slowly cooled down to liquid-nitrogen temperature and transferred to a quartz Dewar. Polarization measurements were performed on a Hitachi–Perkin–Elmer 139 uv-Vis spectrophotometer equipped with polarizers. In most cases uv irradiation of the crystals was carried out with a super-high-pressure mercury arc, type HPW 125 W, but sometimes filtered light from an SP-500 Philips high-pressure mercury arc was used.

ESR Measurements

Unlike the ESR spectra of irradiated TPH powders which can at least be explained qualitatively (see Fig. 2), ESR spectra of irradiated single crystals under the

[1] N. Hirota and S. I. Weissman, Mol. Phys. **5**, 537 (1962); Y. Kirota, J. Chem. Phys. **41**, 3926 (1965); K. H. Hausser and J. N. Murrell, *ibid.* **27**, 500 (1957); T. J. Schaafsma and J. Kommandeur, Mol. Phys. **14**, 525 (1968); M. Itoh and S. Nagakura, Chem. Soc. Japan **40**, 3959 (1967); J. A. McRae and M. R. Symons. J. Chem. Soc. **B4**, 428 (1968); P. D. Bartlett and J. M. McBride, Pure Appl. Chem. **15**, 89 (1967); D. A. Wiersma and J. Kommandeur, Mol. Phys. **13**, 241 (1967).

[2] P. Kottis and R. Lefebre, J. Chem. Phys. **39**, 393 (1963); P. Kottis and R. Lefebre, *ibid.* **41**, 379 (1964); E. Wasserman, L. C. Snyder, and W. A. Yager, *ibid.* **41**, 1963 (1964).

[3] D. A. Wiersma and J. Kommandeur, Mol. Phys. **13**, 241 (1967).

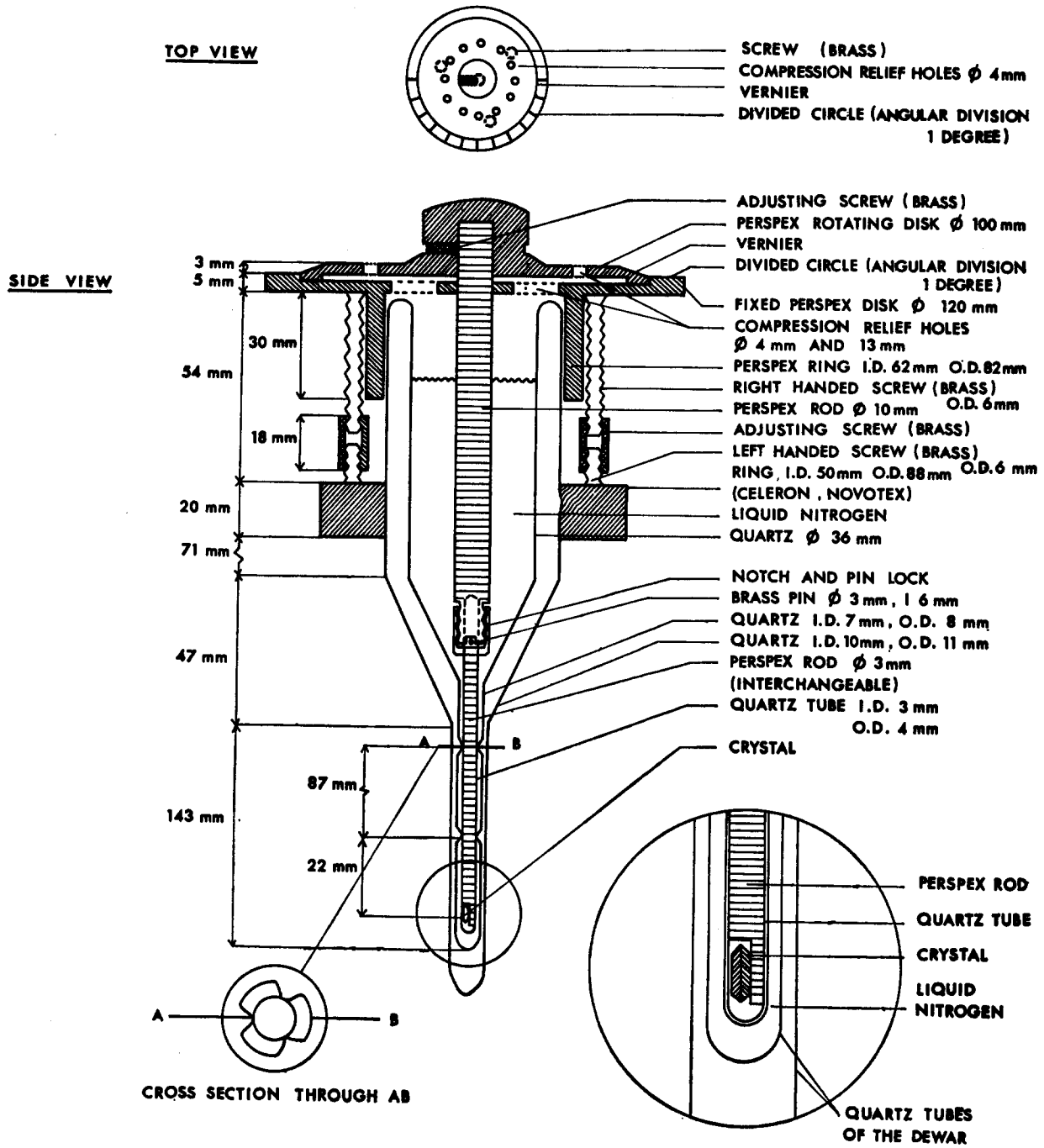


FIG. 1. Quartz Dewar for angularly dependent ESR measurements.

same conditions have quite a complex appearance as is shown in Fig. 3. As is well known now[4] each triplet–radical pair formed through dissociation of a TPH molecule yields two anisotropic ESR lines around $g=2$. A glance at Fig. 3 makes it immediately evident that there are several distinct radical pairs and therefore it is of importance to discuss the crystal structure of TPH first, before going into the details of the ESR spectra arising from the radical pairs.

Crystal Structure of TPH[5]

Tetraphenylhydrazine crystallizes in the $C222_1$ space group with eight molecules per unit cell. From ESR

[4] C. A. Hutchison Jr. and B. W. Mangum, J. Chem. Phys. **34**, 980 (1961).

[5] We are indebted to Professor Vos and Mr. Hoekstra of the Laboratory for Structural Chemistry of this University for their help in obtaining the subsequent information.

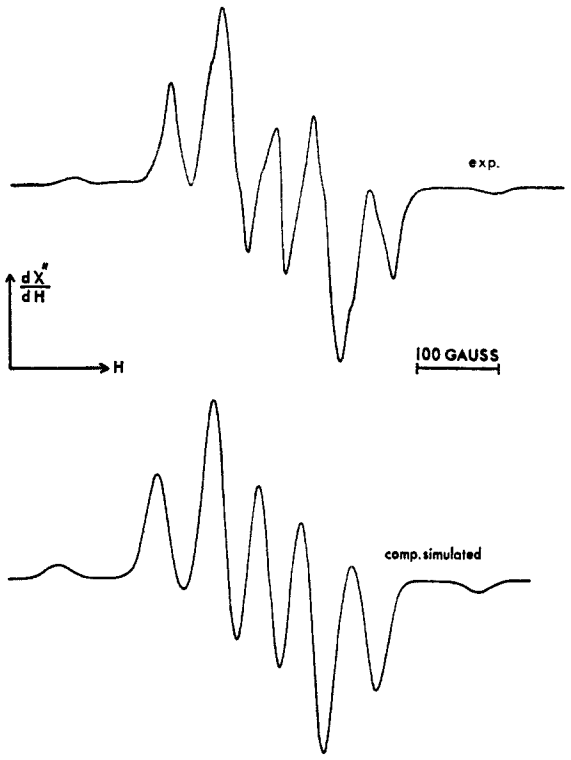


FIG. 2. ESR spectrum of uv-irradiated tetraphenylhydrazine powder at 77°K and its computer-simulated spectrum. The computer-simulated spectrum involves two dipolar split spectra with $D=2.41\times10^{-2}$ cm^{-1} and $D=1.12\times10^{-2}$ cm^{-1} and a radical signal at $g=2$ in the ratio 7:10:9, respectively.

and x-ray measurements it became clear that there are two independent sets of units per unit cell, not connected by translation or interchange symmetry elements. A unit is half a molecule of TPH. Each independent unit generates through the symmetry operations of the space group, seven other units, together forming four TPH molecules. There are thus two classes of TPH molecules, which will be further referred to as α and β molecules.

The best fit with our experiments was obtained, assuming that these two independent classes of molecules occupy special positions around the a and b axis. The β molecules are situated in such a way that the N–N direction is perpendicular to the a axis of the unit cell, the α molecules are situated in such a way that their N–N direction is perpendicular to the b axis of the unit cell. The inclination of the α and β species with respect to the ab plane is unknown. This is illustrated in Fig. 4. The TPH molecule in the crystal thus has at least internal C_2 symmetry. It is of importance to note that the α and β species have different crystalline environments.

Furthermore we will assume that the various magnetically different but configurationally equivalent radical pairs (e.g., the four α-radical pairs of the same configuration) are connected by the same interchange symmetry elements as the undissociated molecules. After dissociation the site character of a symmetry element may be lost but the interchange character of this element is retained. For instance, before dissociation, a TPH molecule has C_2 site symmetry, after dissociation this site symmetry of the formed radical pair may be lost, while still the twofold axis can act as an interchange symmetry element, i.e., relate the spatially different radical pairs.

If we regard the radical pair as an excited state of the TPH molecule, the previous assumption is in accord with the recent work of Kopelman.[6] However, Kopelman proved this "interchange-symmetry concept" for one independent unit, while we made the extension to two dependent units. That this is allowed can be seen from the following consideration. The four α- and β-TPH molecules in a unit cell can be generated through the symmetry operations of the space group from an α- and a β-TPH molecule as well as from two units. Therefore, the molecules are related by the same symmetry operations of the space group as the units (half a molecule).

The radical pairs formed will thus be connected by the same interchange-symmetry elements as the molecules. Since the interchange-symmetry elements relate the spatial orientation of the "defects" in the crystal lattice, they will also relate quantities attached to the molecular frame such as electronic transition moments, the zfs tensor of the radical pairs etc. In other words, the interchange-symmetry elements commute with every part of the total Hamiltonian, e.g. $[R(\text{interchange}), H(\text{spin})]=0$. The fact that the spin-Hamiltonian can be carried over from one radical pair to another is a very useful result as will be shown.

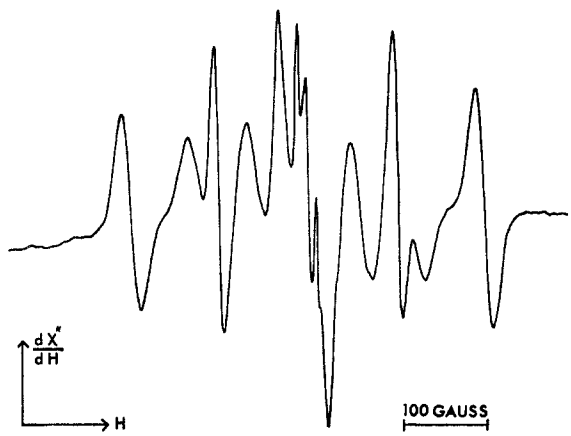


FIG. 3. ESR spectrum of a single crystal of TPH irradiated with unfiltered light from an SP-500, for the magnetic field in the ac plane at 20° from the a axis.

[6] R. Kopelman, J. Chem. Phys. **47**, 2631 (1967).

Single-Crystal ESR Measurements

Since each of the DPA radicals which is formed by breaking of the N–N bond of a TPH molecule has an electron spin, the radical dimer can formally be treated as a two-spin system which forms a triplet and a singlet state. The ESR measurements on the triplet state can be performed, the usual spin Hamiltonian being

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{G}\cdot S+S\cdot\mathbf{A}\cdot S+JS_1\cdot S_2,$$

where $\mathbf{G}$ is the G tensor, $\mathbf{A}$ the spin–spin interaction tensor, and J a constant with the magnitude of the singlet–triplet separation, $S=S_1+S_2$. As is well known[4] this Hamiltonian gives rise to two anisotropic ESR lines for the $\Delta m=1$ transitions, the distance between the lines being independent of J as long as no singlet–triplet mixing occurs, and of $\mathbf{G}$. It can be shown that without any approximation with the magnetic-field vector in an arbitrary direction with respect to the triplet principal axes system, the distance between the two connected $\Delta m=1$ absorptions depends only on the tensor elements of Λ. As was shown before Λ, which is attached to the radical pair frame, can be carried over from one triplet–radical pair to another by the interchange-symmetry operations as long as these radical pairs are configurationally equivalent. This was our starting point in the analysis of the experimental ESR spectra.

Consider one type of radical dimer. For an arbitrary magnetic-field direction, we expect from the number of molecules in a unit cell, to find a maximum of four magnetically inequivalent dimers yielding four sets of ESR lines. With the magnetic-field vector in a symmetry plane this number reduces to two.

When the magnetic field is rotated in this symmetry plane (*ab*, *ac*, or *bc* crystal plane) the ESR splittings should be symmetric around the crystal axis. Realizing that all the crystal axes act as C_2 interchange-symmetry elements the following relation for the splittings can be derived for the two sets (see Appendix):

$$\Delta H_j(\lambda)=\tfrac{1}{2}(\Lambda_{ii}'+\Lambda_{kk}')\pm\Lambda_{ik}'\sin2\lambda+\tfrac{1}{2}(\Lambda_{ii}'-\Lambda_{kk}')\cos2\lambda, \quad (1)$$

where ΔH_j is the observed splitting between two lines, j the crystal axis of rotation, Λ_{ij}' are the elements of Λ with respect to the crystal axes system, and λ is the angle between the magnetic field and the i axis ($i, j=a, b, c$). In practice we made a computer fit to Relation (1) with the measured splittings, excluding in this way orientation faults around the axis of rotation. An ESR spectrum of a single crystal of TPH irradiated with 3650-Å light is shown in Fig. 5 and should be compared with a similar ESR spectrum of a crystal shown in Fig. 3 where unfiltered uv light was used, demonstrating the wavelength dependence of the generation of the radical pairs. For both spectra, the crystals were mounted in the same orientation. For the two sets of most intense peaks of Fig. 5, Figs. 6 and 7 show the measured ESR splittings around the *b* and *c* axes and the computer-fitted curves to Relation (1). In principle one can get all tensor elements of Λ' for one type of radical dimer through rotating the crystal around the different crystal axes. If all tensor elements are known, the eigenvalues and eigenvectors of the spin–spin interaction tensor (zfs tensor) can then be found through a diagonalization procedure. A difficulty arises through the fact that in the employed procedure only the absolute values of the tensor elements are known. The resulting eight tensors, only differing in sign of the tensor elements, yield two independent solutions after the diagonalization procedure. Because both solutions are physically acceptable no *a priori* choice could be made. Through prediction, with both sets of parameters, of the angular dependence of the absorptions around an *arbitrary* rotation axis we were able to discriminate between the two solutions. As the most intense peaks of Fig. 6 show almost their maximum splitting in rotation around the *b* axis, we concluded that these radical dimers arise from dissociation of α-TPH molecules. We call these radical dimers α_1-radical dimers (compare Fig. 5). The fact that in rotation around the *C* axis four anisotropic lines are found indicates that after dissociation of an α-TPH molecule the internal C_2 symmetry is lost. This can be seen remembering that for the magnetic field vector in the *ab* plane the undissociated α-TPH molecules are magnetically equivalent. When after dissociation the internal C_2 symmetry would be retained, the radical dimers would also be magnetically equivalent for this magnetic-field direction. In that case only two absorptions would be expected.

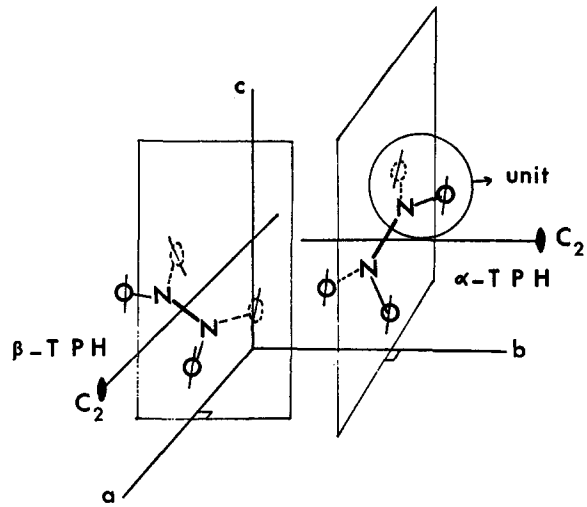


FIG. 4. Orientation of the crystallographically independent TPH species with respect to the crystal axis system.

After rotation around the *b* and *c* crystal axes only

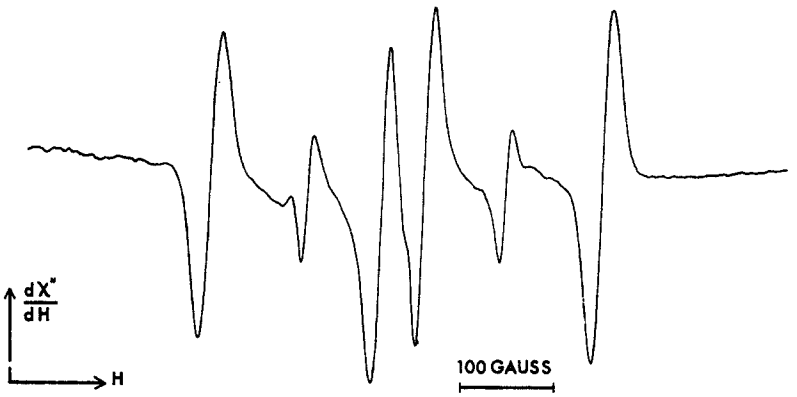


FIG. 5. ESR spectrum of a single crystal of TPH irradiated with 3650-Å light from a superhigh-pressure mercury arc type HPW 125 W for the magnetic field in the *ac* plane at 20° from the *a* axis.

one unknown tensor element is left. In principle one can get this tensor element from a rotation around the *a* axis. For the α_1-radical dimer this was impossible, partly because the missing tensor element was small, giving overlapping absorptions, but the most serious problem was the interference of absorptions arising from other radical dimers. To solve the problem we used a trick. It appeared that after a reasonable guess of the missing tensor element the largest eigenvector of the zfs tensor was almost independent in *orientation* and *magnitude* of this missing tensor element. The ESR splittings observed during rotation around this principal axis (Z axis) are, on the other hand, certainly dependent on the magnitude of this missing tensor element. We therefore rotated the crystal around this principle axis (Z axis) and compared the ESR splittings observed with those predicted for a range of values of the unknown tensor element. In Fig. 8 the experimental observed splittings are shown together with the best-fitting computer predicted curve, where a value of 38 G has been assumed for the unknown tensor element. This value has further been accepted for the computation of the zfs parameters. Because the rotation axis used in this particular experiment was not

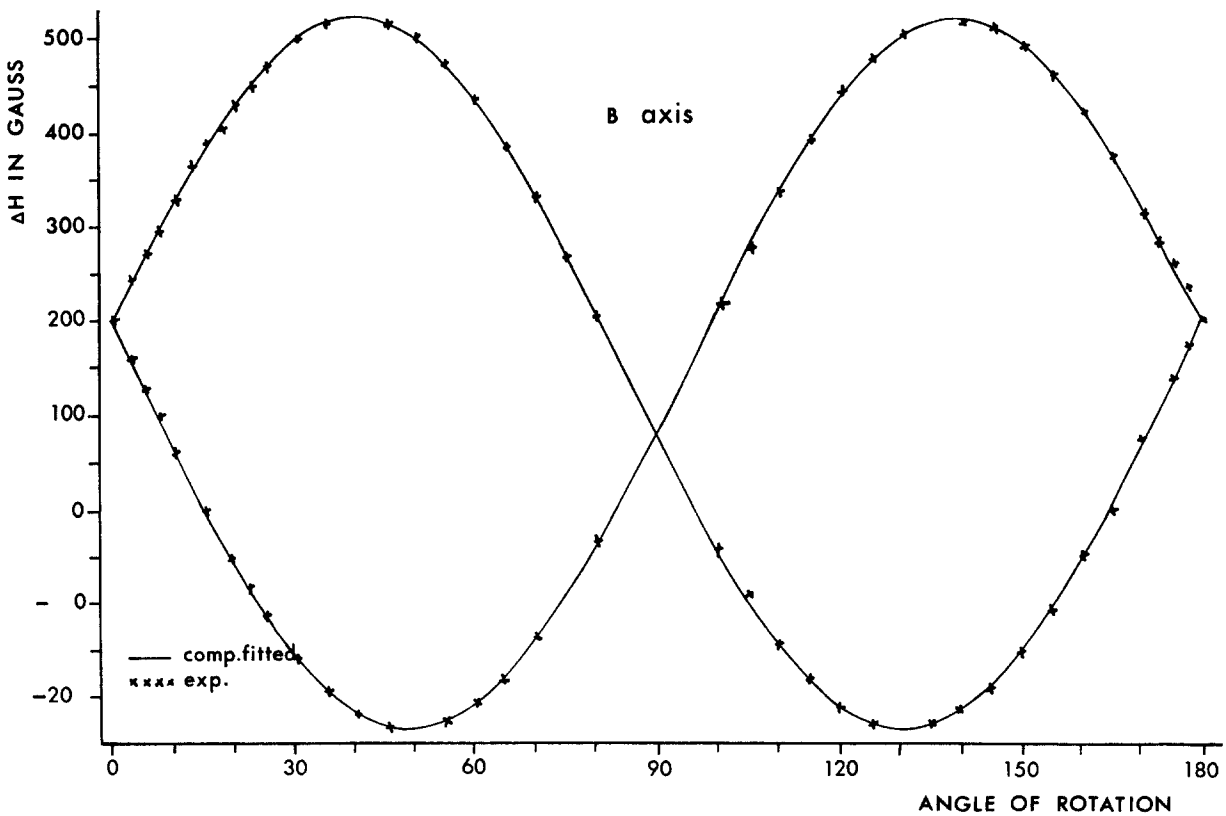


FIG. 6. Experimental ESR splittings observed for rotation around the *b* axis and the computer-fitted curve to Relation (1).

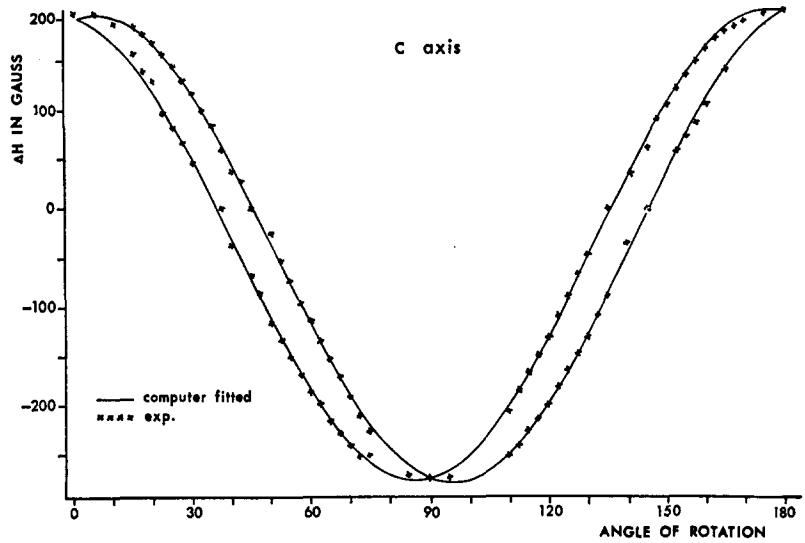


FIG. 7. Experimental ESR splittings observed for rotation around the c axis and the computer-fitted curve to Relation (1).

a crystal axis, the four α_1-radical pairs became magnetically inequivalent as can be seen from the number of lines shown in Fig. 8 (compare Figs. 6 and 7).

Returning to Fig. 5 we see some other less intense pairs of absorptions arising from other radical dimers. In fact there are four of these absorptions, but the other two are hidden under the central intense peaks. The maximum splitting of these ESR lines reaches also its highest value in rotation around the b axis and therefore must also arise from dissociated α-TPH molecules. We call them α_2-radical dimers. The fact that their zfs parameter D is only half of the zfs D of the α_1-radical

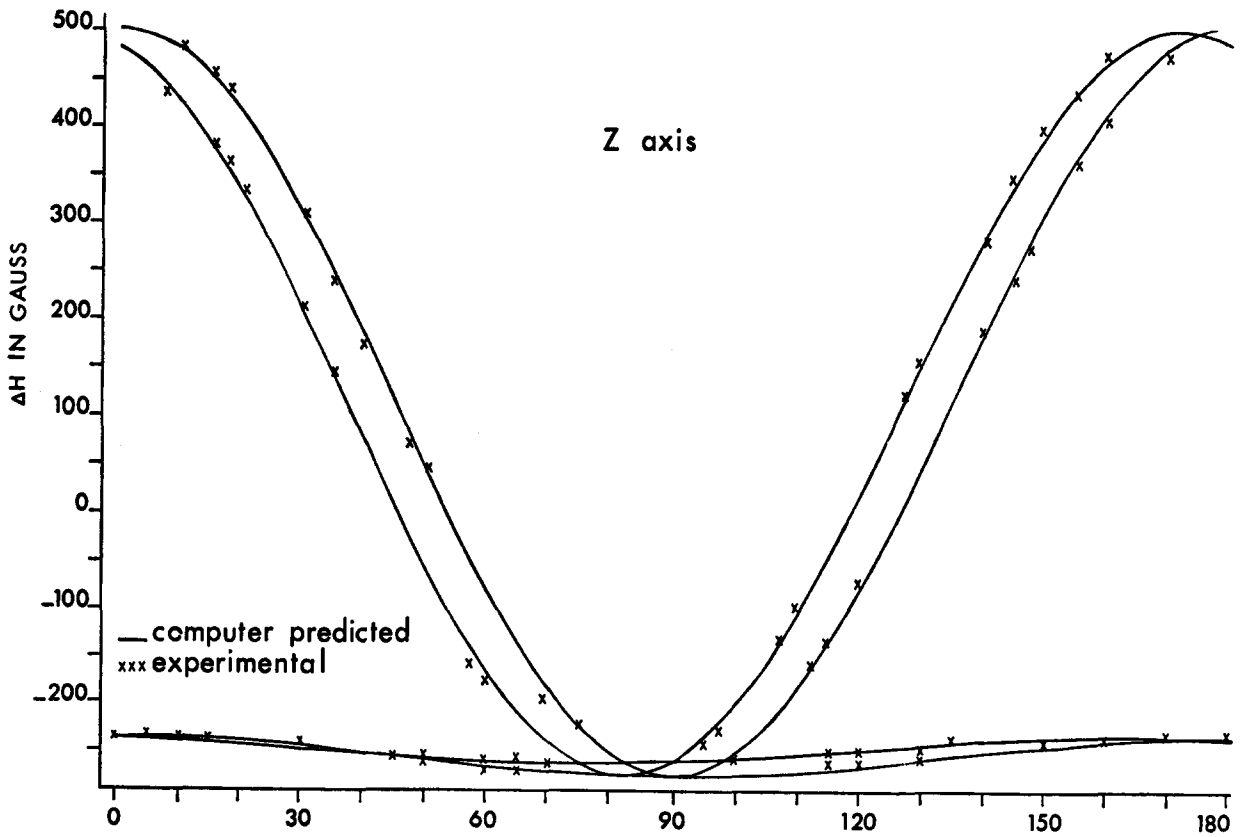


FIG. 8. Experimental observed ESR splittings and the best-fitting computer predicted curve for rotation around the principal tensor axis (Z axis).

TABLE I. Zero-field parameters of eight radical pairs.

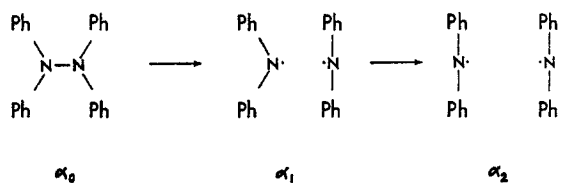
	D 10^{-2} cm^{-1}	E 10^{-4} cm^{-1}	θ_z	φ_z	θ_x	φ_x
α_1	2.416±0.011	6.56±1.0	49°30′±13′	−5°10′±20′	96°±4°	90°±4°
α_2	1.164±0.002	5.0±0.4	52°18′±02′	5°27′±37′	81°±3°	−78°±2°30′
β_1	2.41	5.4	59°			
β_2	1.25	2.2	60°	All z axes of the β dipoles in the bc plane		
β_3	2.24	7.5	54°			
β_4	1.21	7.5	60°	All x axes of the β dipoles along the a axis		
β_5	2.15	<7.5	54°			
β_6	~1.21	<7.5	60°			

dimer indicates that their internal separation is larger. An α-TPH molecule thus can dissociate into two configurationally distinct radical pairs.

From Fig. 3 it can be seen that there must still be some other radical dimers to account for such a large number of ESR lines. These radical dimers are formed through dissociation of β-TPH molecules. Probably, because of the environment of the β-TPH molecules is different from that of the α-TPH molecules they dissociate only appreciably after irradiation with uv light of a shorter wavelength.

The tensor elements of the β-radical pairs were obtained in a manner quite similar to that used for the α pairs, be it that the accuracy obtained was less. The eigenvectors, with respect to the crystal axes system and the eigenvalues, expressed in the zfs parameters D and E of all configurationally different radical pairs are given in Table I.

Our experiments show that through dissociation of β-TPH molecules six configurationally different radical pairs are produced. An interesting aspect of the β-radical dimers is, as far as we could resolve the spectra, that they have internal symmetry C_2, just as before dissociation. This is in contrast with the α-radical dimers. The inclination of the Z axis of the α- and β-radical pairs with the ab plane is quite different. The internal C_2 symmetry of the β-radical dimers was derived from the number of ESR lines observed during rotation around the b axis. In this case only two absorptions were seen. This is only possible when all β-radical dimers are magnetically equivalent for the magnetic-field vector in the ac plane, which is consistent with internal C_2 symmetry.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the photodissociation of the closely related dicarbazyl, where the carbazyl halves cannot become linear is orders of magnitude lower than that of TPH. Since the TPH molecules are fairly tightly packed in their lattice, upon dissociation we do not expect a translation of the centers of mass of the DPA halves, but only a reorientation of the nuclei of one-half around its center of mass. After rupture of the N–N bond a vibrational stretch of one-half as well of both will thus lead to formation of a radical pair. We now have a model to explain the two types of radical pairs. As depicted in Fig. 9 a radical pair can be formed by letting one DPA half stretch (α_1), while another one is formed by letting the two-halves stretch (α_2). We take for the TPH molecule a D_{2d} configuration with sp_2 hybridization at the nitrogen nucleus, and the axes of the benzene rings on one side in a plane orthogonal to the plane containing the axes of the benzene rings on the other side. (Compare the D_{2d} configuration of the α_2-radical pair as shown in Fig. 10.)

Using normal bond lengths and not allowing the centers of mass to move, we find for the N–N distance in α_1: 2.72 Å and in α_2: 3.99 Å. Using the SCMO calculation described earlier[3] for the computation of the spin densities in the triplet state we compute for the α_1-radical pair (sp–sp_2 configuration) $D=2.49\times10^{-2}$ cm^{-1} and for the α_2-radical pair (sp–sp configuration) $D=1.22\times10^{-2}$ cm^{-1} which is in nice agreement with the experimental values of D reported in Table I. (It is of some importance to note here that these results only follow when one takes the redistribution of the electrons into account upon closer approach of the two-halves. A simple calculation on the r^{-3} dependence for two point spins would not have yielded these results.)

There thus appears to be a straightforward explanation for the occurence of two sets of radical pairs. Obviously the reorientation of the nuclei around the centers of mass can occur in a number of ways, presumably also by rotations around them as is evidenced by the various values of E that have been found within any one set. A number of other properties of the radical dimers can also be explained on the basis of our mechanism.

(a) At temperatures between 130°–180°K the α_1 pairs convert into α_2 pairs. α_2 pairs however do not convert into α_1. Apparently, stretching of the other half can be achieved thermally.

(b) At still higher temperatures complete recombination to TPH takes place. Bending vibrations with fairly large amplitude around the C–N–C bond can easily bring this about in our model.

(c) At 77°K photorecombination occurs with visible light absorbed in the charge-resonance band (see below). This "bleaching" phenomenon occurs through the degeneration of the electronic energy into the vibrational modes of the two-halves and their concomitant excitation. A more quantitative discussion of these phenomena will be published elsewhere.[7]

The Conformation of the Radical Pairs

Some information on the relative orientation of the radicals can be extracted from the ratio of the parameters E and D. To this end this ratio was calculated for an α_1-radical pair (sp–sp_2 configuration) and for an α_2-radical pair (sp–sp configuration) changing the conformation of the radical pairs in the way indicated in Fig. 10, computing the E/D ratio every five degrees.

For the distances between the radicals have been taken those values computed from the "vibrational-stretch dissociation mechanism" as discussed before. The limitation of this calculation is that at all angles the same spin-density distribution has been used[8] as the one that had been calculated for the conformation at zero degrees.

D and E have been calculated in the usual fashion.[3] As shown in Fig. 10, E reaches a maximum of 10% of D at a 0° conformation for both radical pairs. An interesting feature of the E/D ratio of the α_1-radical pair is that E changes sign near 55°. Thus without any symmetry E accidently may become zero. From the experimentally found E/D ratio an "angle between the radicals" can be derived from Fig. 10. For the α_2 radical pair this angle is 50°, while for the α_1-radical pair this angle is 45° or 70°. Since the absolute signs of D and E are unknown, we must make a choice. If we choose 45°, we have almost the same angle as in the α_1 pair. Unfortunately, the angle in the parent TPH molecule is as yet unknown. Molecular model studies indicate that 45° is not an unreasonable value. This then can be taken to mean that only the N–N stretch vibration is involved in the dissociation process.

In general we can conclude that the absolute values of D and the values for the E/D ratios support the dissociation mechanism proposed.

Comparison with Solid Solution

It is of some interest to compare the single-crystal studies with those on solid solution spectra. Evidently in solution only radical pairs of the α_2-type are formed,[3] a lot of information being lumped together in the linewidth of the ESR absorptions.

However, the usefulness of computer simulations is beautifully demonstrated. From computer-simulated ESR spectra of radical pairs in solid solution we were able to derive a maximum value of E of about 5.6×10^{-4} cm^{-1}. This value is in good agreement with the average value of E obtained from ESR single-crystal measurements for α_2-type radical pairs.

[7] D. A. Wiersma and J. Kommandeur (unpublished).

[8] This assumption is probably not too bad since almost the same curves are obtained in Fig. 10 if we start from the spin-density distribution in a 90° conformation.

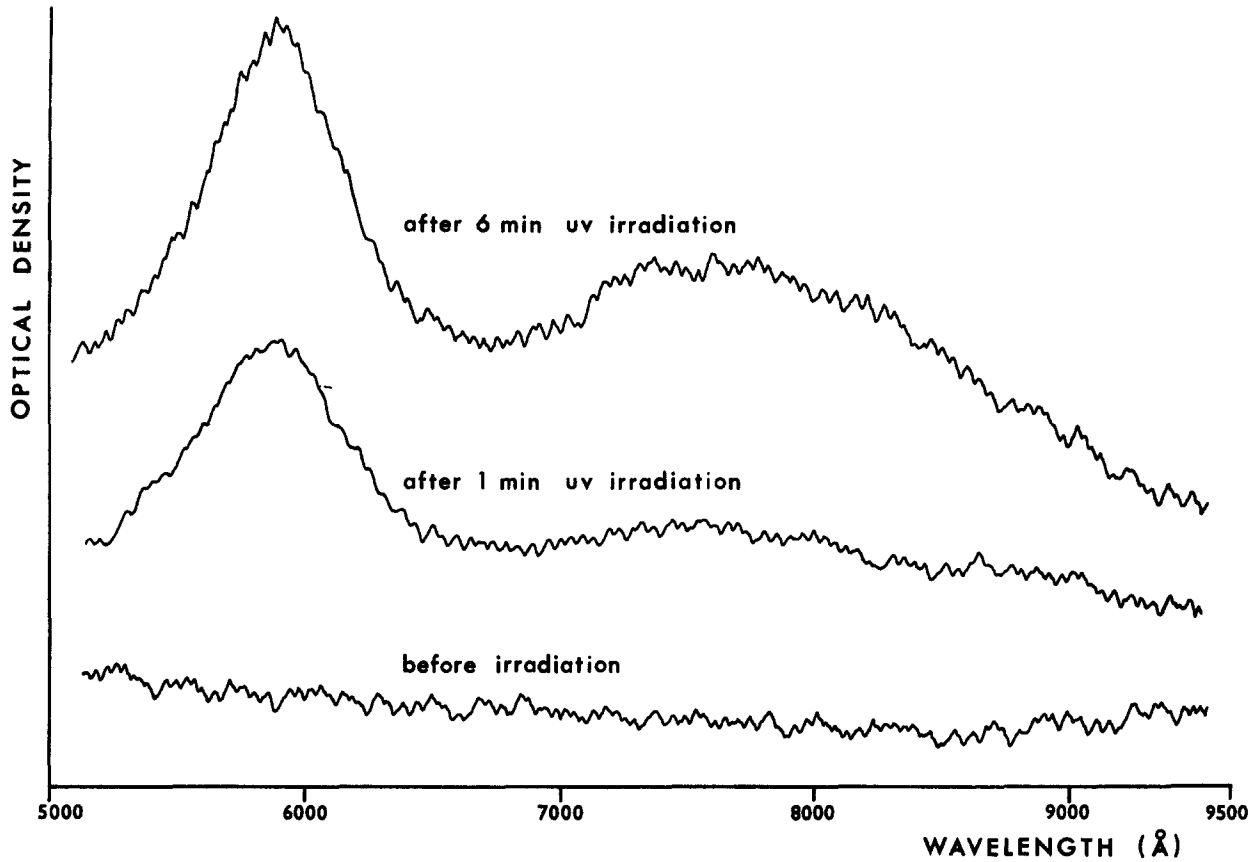

FIG. 11. Visible absorption spectra of TPH before and after irradiation with 3650-Å light from a superhigh-pressure mercury arc.

Optical Measurements

The Electronic Absorption Spectra

In Fig. 11 the visible absorption spectrum of a single crystal of TPH before and after uv irradiation is shown. As is evident from this figure two absorptions arise: one at 6000 Å (2.06 eV) and after irradiating for longer times one at about 7500 Å (1.65 eV). The fact that these bands do not appear simultaneously implies that they arise from two different species. Through comparison with ESR spectra the 6000-Å band was identified as arising from α_1- and the 7500-Å band as arising from a_2-radical dimers. The 3-Å β-radical dimers were shown to absorb at 5600 Å (2.22 eV) and the 4-Å β-radical dimers at 8000 Å (1.55 eV). The appearance of these bands can easily be explained based on a radcal dimer model.

Two types of wavefunctions can be formed in the VB scheme[9]: singlets $^1\Psi_0(R_1^{\cdot}, R_2^{\cdot})$ and triplets $^3\Psi_0(R_1^{\cdot}, R_2^{\cdot})$. A charge-transfer state, where one electron is transferred from one radical to the half-occupied orbital of the other radical will be close in energy to the ground state. By virtue of the symmetry of the system, two charge-resonance states, a symmetrical, and an antisymmetrical state exist,

$$\phi_{CT}^{\pm}=2^{-1/2}[^1\Psi_1(R_1^+, R_2^-)\pm{}^1\Psi_1(R_1^-, R_2^+)].$$

It is obvious that the triplet charge-resonance states will be much higher in energy. When there is overlap between the π-molecular orbitals of the radicals the zero-order singlet function $^1\Psi_0(R_1^{\cdot}, R_2^{\cdot})$ will mix with the symmetrical charge-resonance state, lowering the energy of the singlet state relative to the triplet state. The absorptions observed must be assigned to a transition from the ground state, $^1\tilde{\Psi}_{1g}=a^1\Psi_0(R_1^{\cdot}, R_2^{\cdot})+\lambda\phi_{CT}^+$ to the antisymmetrical charge-transfer state ϕ_{CT}^-, a so-called charge-resonance transition.[10] Even a simple SCMO calculation on a radical dimer yields such a charge-resonance absorption,[8] since the self-consistent-field formalism is formally equivalent to a first-order configuration interaction[11] and thus includes the ground-state interaction with the symmetrical charge-resonance state. A definite assignment of the visible and near-infrared absorptions as discussed before to charge-resonance absorptions can only be based on polariza-

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[11] L. Brillouin, *Les Champs Self-consistent de Hartree et de Fock* (Hermann & Cie., Paris, 1939).

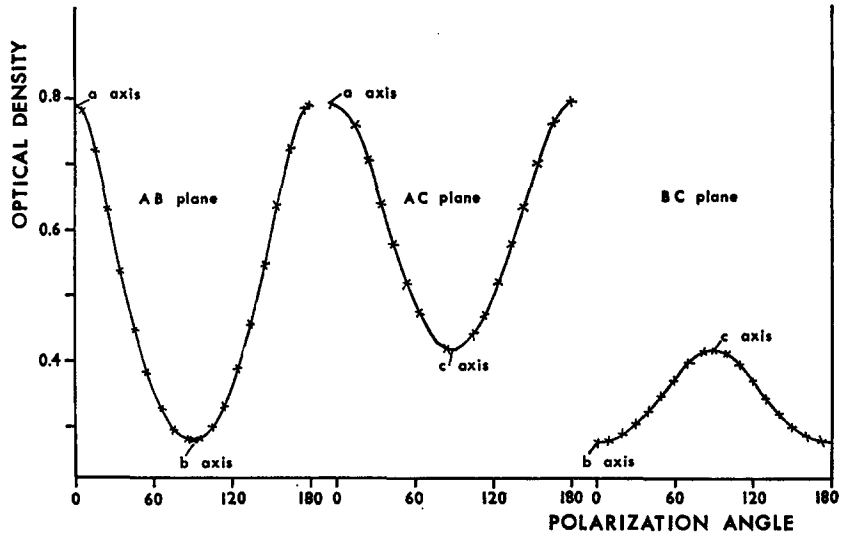

FIG. 12. Polarization of the absorption at 6250 Å.

tion measurements. From the fact that the spin density on the nitrogen nucleus is high, we identify the largest zfs and therefore the z axis of the zfs tensor as the N–N direction between the two radicals.

For a charge-resonance transition we expect that the transition moment at least has a finite component along this axis. At this point we stress the fact that there is no *a priori* reason for the coincidence of the eigenvectors of the zfs tensor and the electronic transition moments because of the lack of symmetry of the α-radical pairs.

Polarization Measurements

Polarization measurements were performed under conditions where mainly α_1- and α_2-radical pairs were present. In Fig. 12 the results of these measurements are shown for the α_1-radical pairs. From these measurements polarization ratios can be derived of about 3:1:1.6 for the a, b, and c axis, respectively. For α_2-radical pairs these ratios are 1.5:1:1.7. These values were taken at 6250 and 7750 Å, respectively, where the polarization ratios as a function of wavelength showed extrema. These polarization ratios show that the absorption is appreciable in a direction along the z axis of the zfs tensor. This is consistent with the assignment of a charge-resonance absorption. Without correcting for light scattering for both radical pairs, an angle of 35° between the transition moment and the z axis of the zfs tensor is obtained. That scattering occurs is illustrated by Fig. 11, where the base line seems to shift upwards in the successive spectra. This scattering may be due to a disturbance of the crystal lattice as a result of the photodissociation process.

Singlet–Triplet Splittings

As was discussed before, the radical dimer may be formally treated as a two-spin system, which forms a triplet and a singlet state. The magnetic properties arise from the triplet state and the optical properties from the singlet state. The energy gap between the two states and the assignment of the ground state may be derived from temperature-dependent measurements. For an isolated two-spin system the integrated intensity of the ESR absorption should vary as[12]

$$T^{-1}[1+\tfrac{1}{3}\exp(J/kT)]^{-1}, \qquad (2)$$

where T is the absolute temperature and J the energy difference between the singlet and triplet state. As long as the linewidth of the ESR signal remains constant at different temperatures the integrated absorption intensity should be proportional to the height of the derivative of the ESR signal.[13]

Since we did not observe any change in linewidth at different temperatures we measured the height of the signal. For a system of singlets and triplets the susceptibility χ goes through a maximum at $Tm \approx 0.625 \times J/k$. Therefore, on cooling, some radical dimer lines with low J increase and some radical dimer lines with high J decrease in intensity. This is illustrated in Fig. 13.

TABLE II. Singlet–triplet splittings.

Radical pair	J (cm^{-1})	D 10^{-2} (cm^{-1})
α_1	132±4	2.42
α_2	41±3	1.16
$\frac{1}{3}(\beta_2+\beta_4+\beta_6)$	33±4	1.22
β_1	>80	2.41

[12] D. B. Chesnut and P. Arthur, Jr., J. Chem. Phys. **36**, 2970 (1962).
[13] D. B. Chesnut and W. D. Phillips, J. Chem. Phys. **35**, 1003 (1961).

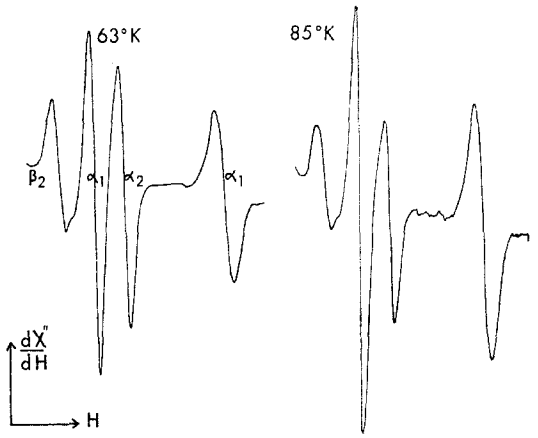

FIG. 13. Temperature dependence of the ESR signals of some radical pairs.

With Relation (2) as the relation that describes the temperature dependence of the paramagnetism we are able to derive from signal-intensity measurements at two different temperatures singlet–triplet separations and make the assignment of the ground state of all radical pairs as the singlet state.

In Table II the measured singlet–triplet splittings are collected, together with the D values taken from Table I. In a simple two-electron model, the singlet–triplet splitting J is for the same orbital configuration equal to the exchange interaction energy of the two electrons involved:

$$J=2\int a(1)b(2)r_{12}^{-1}a(2)b(1)d\tau,$$

where a and b are the half-filled MO's of the radicals and the integration has to be performed over spin and space coordinates of both electrons.

This simple model fails here because of the importance of charge-resonance states. As was shown in "The Electronic Absorption Spectra section," there will be a lowering of the zero-order singlet ground state relative to the triplet state as a result of the mixing of the zero-order singlet ground state with the symmetrical charge-resonance state. Therefore the energy difference between the zero-order triplet state ${}^3\Psi_0(R_1^{\cdot}, R_2^{\cdot})$ and the ground state ${}^1\tilde{\Psi}_{1g}=a\,{}^1\Psi_0(R_1^{\cdot}, R_2^{\cdot})+\lambda\phi_{CT}{}^+$, $\langle{}^3\Psi_0 \mid H \mid {}^3\Psi_0\rangle-\langle{}^1\tilde{\Psi}_{1g} \mid H \mid {}^1\tilde{\Psi}_{1g}\rangle$, where H is the total Hamiltonian operator, does not yield a simple expression for the energy difference between the singlet and the triplet state. However, when we compare the J and D values of Table II, it is evident that J falls off with larger separation (small D value) between the radicals.

This is in qualitative agreement with the radical dimer model discussed before, since the overlap between the π-molecular orbitals will become larger at smaller interradical separations. This results in more mixing of the charge-resonance state with the zero-order singlet ground state, lowering the singlet state progressively more below the triplet state at smaller radical separations. The difference in J values between 3-Å α- and β-radical pairs again shows their different geometrical structure as was also derived from the measurements of the E/D ratios. The observation that for all radical pairs the singlet state is the ground state is also in agreement with the discussion in the section entitled "The Electronic Absorption Spectra."

CONCLUSIONS

In conclusion we can say that through photodissociation of a single crystal of TPH eight configurationally different radical dimers are found. These dimers are characterized by their single-crystal ESR spectra. All dimers have a singlet ground state, the singlet–triplet splitting depending on the interradical separation and their conformation. They also have a low-lying charge-resonance state, which leads to a polarized absorption in the visible part of the spectrum. A tentative mechanism for the photodissociation suggests that it takes place in two steps, in which first one and then both radicals become linear, the N–N stretching vibration being responsible for the dissociation. Further studies are being carried out to ascertain, whether this mechanism can be extended to other photodissociations.

APPENDIX

When the spin–spin interaction Hamiltonian is written as

$$\mathcal{H}_{ss}=S\cdot\Lambda\cdot S,$$

use can be made of the symmetry operations of the space group of the crystal connecting the spatially different spin–spin interaction tensors Λ. Since the diagonal Λ tensors are related by the interchange symmetry elements, the nondiagonal Λ' tensors (f.i. in the crystal axes system) are also.

Because, in our procedure, we determined the tensor elements of the Λ' tensor in the crystal axes system, it is of interest to know which elements of this tensor can be determined from the observed ESR splittings in the laboratory axes system. Therefore consider a tensor Λ' in the crystal axes system and a tensor Λ'' in the laboratory axes system. The representation of tensor Λ' in the laboratory axes system will be found after a similarity transformation $\Lambda''=R^{-1}\Lambda'R$ with the well-known rotation matrix $R(\alpha, \beta, \gamma)$,[14] where α, β, and γ are the Eulerian angles. The elements of Λ'' can then be computed. For the magnetic field along the x axis, and the z axis as the axis of rotation Λ_{zz}'' is the matrix element of interest. With λ as the angle of rotation round the z axis the separation between the anisotropic ESR lines is given by the relation $\Delta H(\lambda)=\Lambda_{xx}''=$

[14] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Co., Inc., Princeton, N.J., 1956), 2nd ed., p. 286.

$A+B\sin2\lambda+C\cos2\lambda$, where A, B, and C are constants only depending on α, β, and γ and a phase angle. More generally, for a rotation around any crystal axis the following relation is found:

$$\Delta H_j(\lambda)=\tfrac{1}{2}(\Lambda_{ii}'+\Lambda_{kk}')\pm\Lambda_{ik}'\sin2\lambda + \tfrac{1}{2}(\Lambda_{ii}'-\Lambda_{kk}')\cos2\lambda. \quad (1)$$

There are thus two solutions possible if $\Lambda_{ik}'\neq0$. The above derived relation is valid for one tensor Λ' in the crystal axes system. When there are four Λ' tensors in the crystal axes system related by three C_2 axes, it is easy to show that two of them will give the plus sign and the other two the minus sign. However, it is not known which tensors give plus and which give minus signs. In the case under investigation two ESR splittings will be observed which are connected through Relation (1). As is evident from this relation, since $\Delta H_j(90°+\lambda)=\Delta H_j(90°-\lambda)$, there will be a mirror relationship of the ESR splittings observed around any crystal axis. This was shown in Figs. 7 and 8.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 50, NUMBER 7 1 APRIL 1969

Kinetics of the Thermal and Nitric Oxide-Catalyzed Geometrical Isomerization of *cis*- and *trans*-Propylene-1-d_1

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(Received 16 October 1968)

The thermal *cis–trans* isomerization of propylene-1-d_1 has been studied from 460°–541°C over a pressure range of 3–250 mm Hg in a Pyrex reaction vessel. The reaction below 20 mm Hg is homogeneous and unimolecular but just in the pressure-dependent region, $k_{\infty,cis-trans}(\text{sec}^{-1})=10^{13.16}\exp(-61\,300/RT)$. Above 20 mm a second-order reaction begins to contribute to the isomerization rate. The nitric oxide-catalyzed isomerization of *cis*-propylene-1-d_1 was studied between 398° and 452°C at propylene pressures of between 8 and 22 mm. Hg and NO pressures of 5–35 mm Hg. The reaction is first order in propylene and nitric oxide. The second-order rate constant is given by $k(\text{liters mole}^{-1}\cdot\text{second}^{-1})=10^{8.27}\exp(-27\,900/RT)$.

INTRODUCTION

It has become apparent that many of the *cis–trans* isomerizations of substituted ethylenes studied and originally thought to be homogeneous unimolecular reactions were proceeding via a radical mechanism.[1] The number of genuine examples of the geometrical isomerization of substituted ethylenes occurring via a homogeneous unimolecular path is small (see Refs. 1 and 2 for examples). In all of these cases it appears that the measured frequency factor is in agreement with a mechanism in which isomerization occurs via a twisting of the double bond with the molecule remaining in a singlet electronic state, rather than via excitation to a triplet state which, on reverting to the ground state, results in isomerization. The present study provides a further example of an authentic homogeneous unimolecular *cis–trans* isomerization with the frequency factor in agreement with the singlet mechanism.

EXPERIMENTAL

Materials

Preparation of cis- and trans-Propylene-1-d_1

The method used was the one described by Farina and Peraldo.[3] Pure (>98%) *cis*-($bp_{25}-18°C$) and *trans*-($bp_{25}-13°C$) bromopropene were obtained by fractional distillation of the mixed isomers using a 22-in. Podbielniak-type column operated with a head temperature of about −20°C. A catalyzed geometrical isomerization on the column was suppressed by addition of small amounts of ethanol to the mixture. Replacement of bromine by deuterium was effected by reaction with lithium at −12°C in ether solution under an atmosphere of nitrogen and reaction of the compound formed with D_2O. Ether was removed by trap-to-trap distillation. Mass-spectrometric, infrared, and vapor phase chromatographic analysis gave the following results:

cis-propylene-1-d_1 5.4% *trans*-d_1; 2.6% d_0; 0.1% other products,
trans-propylene-1-d_1 2.8% *cis*-d_1; 3.2% d_0; 0.3% other products.

The NMR spectra run on 10% solutions in carbon tetrachloride confirmed the assignment of the *cis* and *trans* configurations.

Preparation of Methane

Methane (Matheson C.P. grade) was degassed by pumping the liquid for several seconds followed by vaporization. This cycle was repeated at least 10 times.

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[2] M. C. Lin and K. J. Laidler, Can. J. Chem. **46**, 973 (1968).
[3] M. Farina and M. Peraldo, Gazz. Chim. Ital. **90**, 973 (1960).